/307
11 :6

Enhanced ClO from 10 to 12 km Near the Winter Polar Tropopause During SOLVE/THESEO-2000

Brett F. Thornton[1], Darin W. Toohey[2], Linnea M. Avallone[2], Hartwig Harder[3], Monica Martinez[3], James B. Simpas[3], William H. Brune[3], and Melody A. Avery[4]

[1]Department of Chemistry, University of Colorado, Boulder, CO
[2]Program in Atmospheric And Oceanic Sciences, University of Colorado, Boulder, CO
[3]Department of Meteorology, Pennsylvania State University, University Park, PA
[4]NASA Langley Research Center, Hampton, VA

Abstract. Abundances of chlorine oxide have been measured *in situ* near the tropopause from the NASA DC-8 aircraft during the SOLVE/THESEO-2000 campaign. Significant abundances, averaging 15-20 parts per trillion, were observed throughout the lowermost stratosphere at high latitudes during winter. Mixing ratios of ClO generally increased with increasing ozone (the latter an indicator of stratospheric air) as has been observed at other latitudes and seasons. However, the ratio of ClO to inorganic chlorine ($[ClO]/[Cl_y]$) was found to be largest in air characterized by low abundances of ozone (~100-250). It was within this range of ozone values that cirrus clouds were also observed occasionally throughout the measurement period, although distinct enhancements of ClO were not commonly observed directly within cirrus clouds. Elevated abundances of ClO were also apparently observed in polar darkness. However, we attribute these measurements to OClO, a species that can also be detected by the DC-8 instrument under the conditions encountered during SOLVE/THESEO-2000. Using a photochemical box model constrained by daytime abundances of ClO, we infer that BrO mixing ratios in this region were approximately 2-4 ppt, consistent with previous measurements from balloon-borne remote sensors.

Final Report for NASA Project NAG2-1307

In Situ Measurements of Halogen Oxides from the DC-8 for SOLVE

Principal Investigator: Darin Toohey

Co-investigator: Brett Thornton

Organization: Program in Atmospheric and Oceanic Sciences, University of Colorado, Boulder

Collaborators: William Brune
Hartwig Harder
Monica Martinez-Harder
James Simpas
(The Pennsylvania State University)

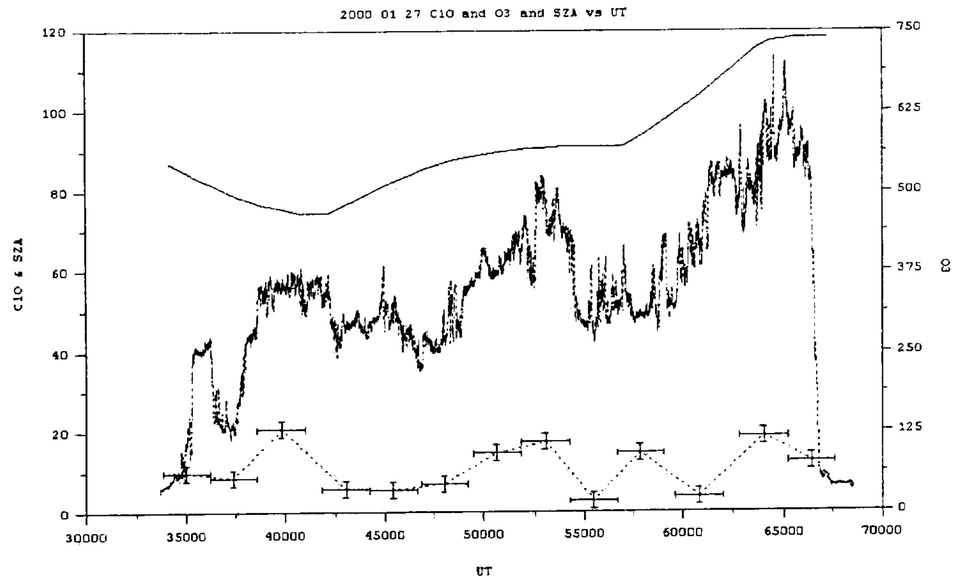
Objectives

This goal of this project was to develop a new instrument to measure ClO and BrO on the NASA DC-8 aircraft during the SOLVE campaign from October 1999 through March 2000. The instrument was integrated into the ATHOS (Penn State) flow system to reduce the cost and the time that would be necessary to develop a completely new instrument. The instrument was successfully integrated onto the DC in November 1999 and the December Kiruna deployment was used to optimize the measurements in the DC-8 configuration. The best measurements were obtained in the two 2000 deployments from Kiruna.

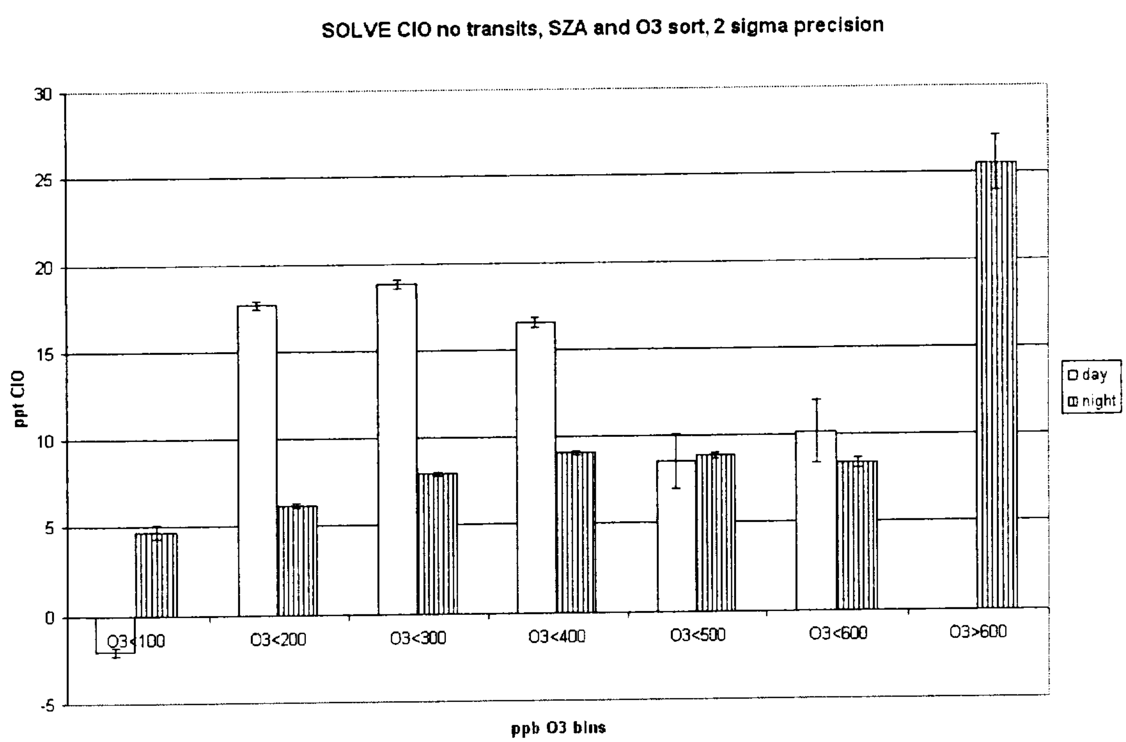
Summary of Results

In the configuration employed on the DC-8, one of the ATHOS detection axes (HO_2) had to be removed to accommodate the ClO and BrO axes. Thus, OH and HO_2 could not be measured simultaneously, but rather in an cycle that alternated with addition and removal of nitric oxide used to convert HO_2 to OH. Similarly, during periods of HO_2 measurements, ClO and BrO could not be measured because of possible wall losses of Cl and Br in the HO_x detection axis. Thus, the duty cycles for the measurements were less than normal. Nevertheless, the measurements proved to be very interesting.

For most of the SOLVE campaign, abundances of ClO observed in the lower stratosphere were in the range 5-30 parts per trillion. An example of the results for one flight (000127) is shown in the figure below.

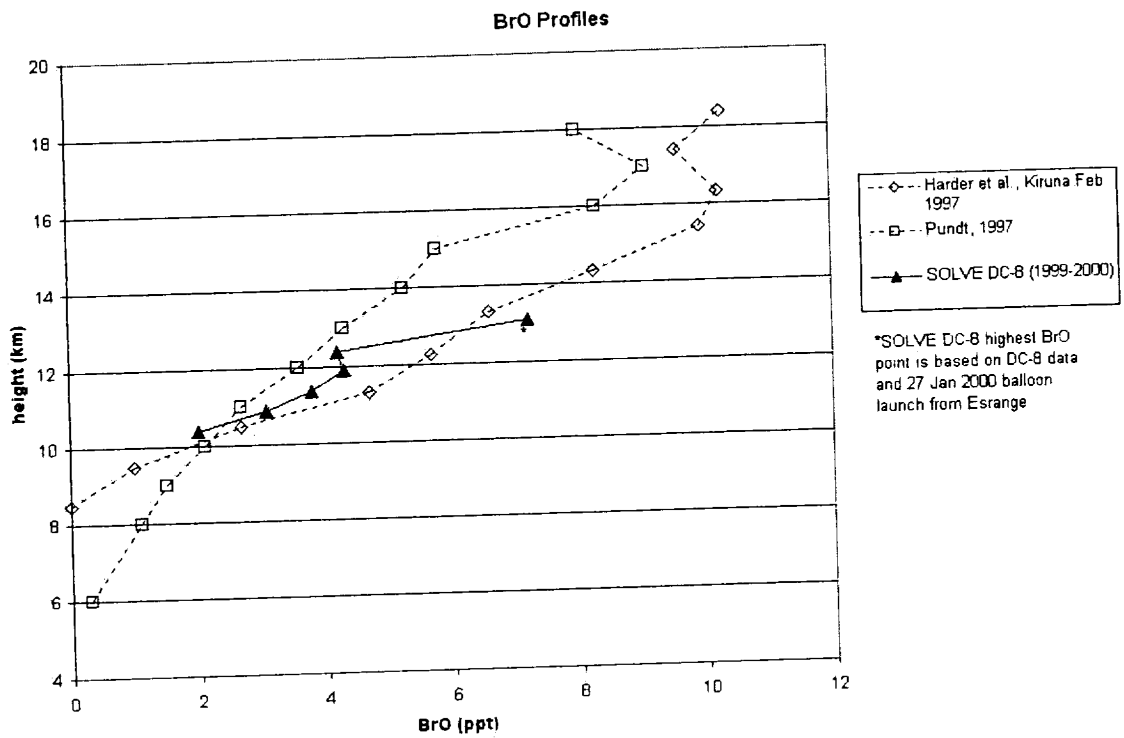


To first order, ClO abundances increased with increasing 'height' (using ozone as a surrogate for altitude height) in the high-latitude lowermost stratosphere. This result is consistent with previous observations at lower latitudes and higher altitudes. However, the abundances of ClO were considerably larger than observed at comparable ozone abundances at lower latitudes. In addition, non-zero abundances of ClO were observed in darkness, as shown in the figure below.



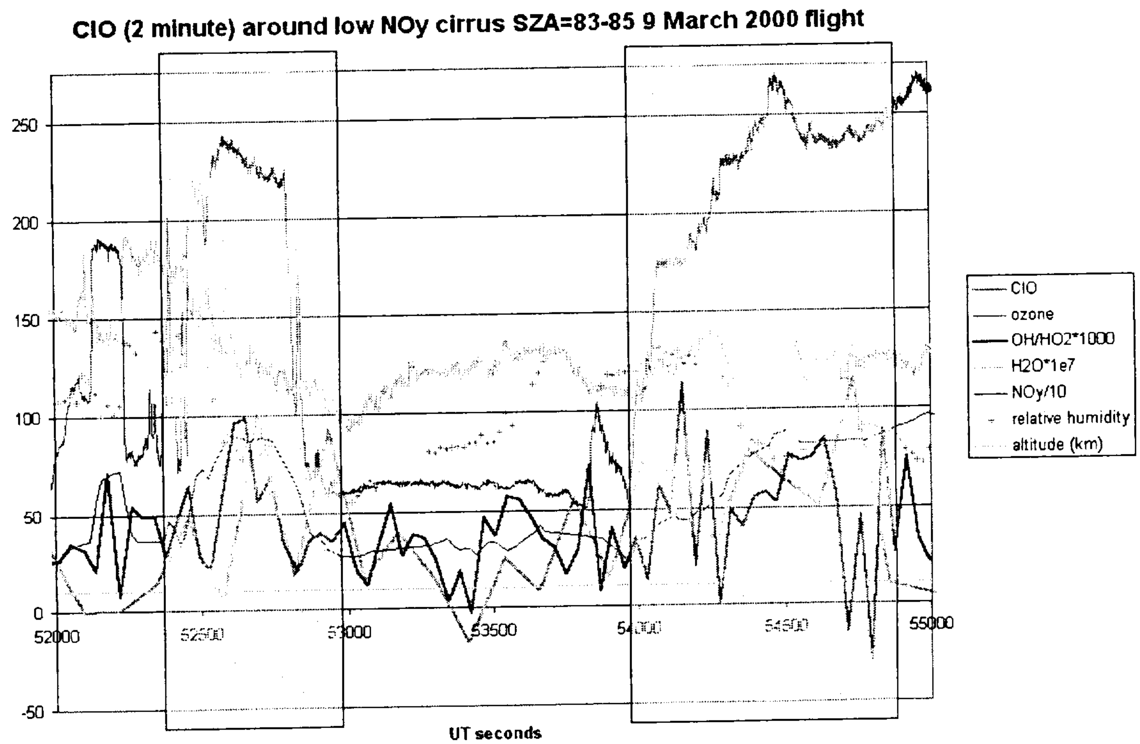
Typically, the value observed at night was less than that under similar conditions (except solar illumination) during daylight. We have interpreted these nighttime signals as being due to OClO, a species that can be detected by our instrument as configured for the DC-8.

Modeling studies of these non-zero signals at night indicate the presence of ~2-4 ppt of BrO in daylight. Together with 10-20 ppt of ClO in daylight, these abundances are sufficient to explain the amounts of OClO that we infer in darkness. These abundances of BrO agree very well with previous reports from balloon-borne remote sensors deployed from Kiruna, Sweden during similar times of year, as shown in the figure below.

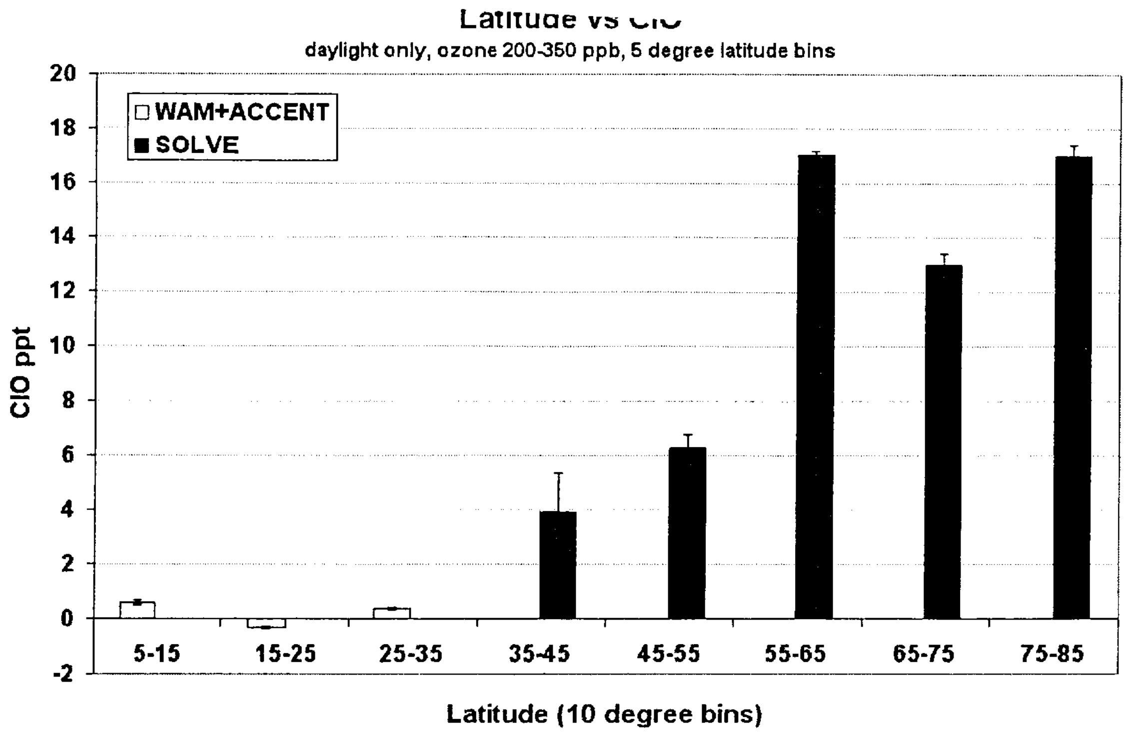


Measurements of BrO on the DC-proved very difficult for several reasons. First, significant portions of flights during the early part of the mission (December/January) were in total darkness, and abundances of BrO were below the detection limit. Second, the low-pressure configuration required for measurements of OH and HO_2 proved detrimental to measurements of BrO, such that very long integration times were needed for adequate signal-to-noise ratios. Never-the-less, non-zero abundances of BrO were detected for most of the flights in daylight. The abundances of BrO determined from the observed signals were in excess of 10 parts per trillion, considerably higher than expected. We do not believe that these measured abundances of BrO are real. Rather, we believe that there is some interference that has contributed a constant offset of 5-10 ppt to the BrO signals. Following several months of intensive laboratory work, we were unable to identify the source of this interference. It is possible that the combination of low temperatures and high abundances of ozone in air sampled by the DC-8 leads to production of an exotic species that fluoresces in the same spectral region as bromine atoms. Unfortunately, shortly after the SOLVE mission, we were forced to vacate our temporary laboratory at CU, and we are still waiting for a replacement laboratory to complete these tests. At this time we can only state that the signals observed in the bromine detection axis on the DC-8 were consistent with the abundances of BrO inferred from the detection of OClO in darkness.

Another result of the SOLVE measurements of ClO was the detection of enhanced values within regions influenced by particles (PSCs and cirrus clouds). Abundances of ClO as high as 70-110 ppt were observed on several occasions within cirrus clouds. However, abundances of ClO were not always enhanced within cirrus clouds. On most occasions, the average abundance within clouds was nearly indistinguishable from abundances outside of clouds. At the present time the explanation for these observations remains unclear. However, the same behavior is apparent in the measurements of OH and HO_2. An example of such behavior is shown in the figure below.



The observations of enhancements of ClO near the tropopause during SOLVE begs the question 'why haven't these enhancements been observed previously by the ER-2 aircraft'? The figure below shows a composite latitudinal distribution ofClO from the SOLVE (DC-8) and WAM/ACCENT (WB-57) campaigns. It is clear from this figure that there is a strong latitudinal gradient in ClO enhancements. Together with the work of Smith et al. (JGR 2001), it appears that the combination of high relative humidities and low sun angles is required to produce ClO enhancements.



Inventions/Patents - There were no inventions or patents as a result of this work.

Publications

The first results from the ClO measurements during SOLVE will be reported in a future publication to be submitted to JGR-Atmospheres. The title and abstract of this manuscript are reproduced on the following page.